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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Viscosity and Phase Separation Control Additives for Foaming Alkyl Aromatic Sulfonates

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ABSTRACT

A foaming surfactant concentrate useful in enhanced oil recovery with improved stability and flowability. This concentrate comprises water, greater than 12 wt % of a C_{20-30} alkyl aromatic sulfonate component having an average molecular weight from about 460 to about 600, a mixture of organic additives comprising a viscosity-reducing hydrotrope and a dispersant comprising a nonionic surfactant, and optionally a polymeric nonionic surfactant. The amount of organic additives is less than 50 wt % of the weight of the C_{20-30} alkyl aromatic sulfonate.

VISCOSITY AND PHASE SEPARATION CONTROL ADDITIVES FOR FOAMING ALKYL AROMATIC SULFONATES

RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Serial No. 07/409,595 filed September 23, 1989.

BACKGROUND OF THE INVENTION

The present invention relates to flowable concentrates of foam forming alkyl aromatic sulfonate surfactants, and the use of these concentrates in steam enhanced oil recovery.

In particular, certain alkyl aromatic sulfonates have been disclosed as surfactants for steam-foam drive systems. See for example, Canadian Patent 1,247,850, which discloses the use of C_{20-24} alkyl aromatic sulfonates.

In general, foaming surfactants are desirably manufactured, transported, and stored in concentrated form prior to being employed in the oil field. Concentrates reduce shipping and manufacturing costs.

There are certain requirements for commercially useful concentrates. To be acceptable, concentrates must possess good handling characteristics and good flow properties, e.g., they should be non-thixotropic, with viscosities of not greater than about 3000 centipoise (cp) when prepared. Furthermore, concentrates need to be stable from phase separation and especially stable under freeze-thaw conditions. Good dispersion stability is desirable to maintain a homogeneous formulation without settling or

separation so the mixtures can be subjected to storage for extended periods and are pumpable.

Unfortunately, with higher molecular weight alkyl aromatic sulfonate surfactants - such as linear C_{20-24} alkyl toluene sulfonates - at concentrations above about 10 wt %, the problems of physical phase instability and high viscosity become almost intractable. Moreover, as the molecular weight of the alkyl group increases from C_{14-18} to C_{20-30}, the concentrates appear to become dispersions of solids rather than mixtures of liquids. It is believed that the problems are due, in part, to the waxy nature of these high molecular weight linear alkyl groups.

It is disclosed in pending application Serial No. 07/409,595, filed September 23, 1989, that when concentrates of alkyl aromatic sulfonates having an average molecular weight of 400-600 are subjected to extended storage (i.e., storage extending from days to several months, generally at temperatures about 70°F) and/or exposure to cold temperatures as would exist in many areas during the winter season (i.e., temperatures of about 20°F), these concentrates display significant increases in viscosity to values greater than about 10,000-15,000. This dramatic increase in viscosity and the resulting reduced flowability make field handling of these concentrates extremely difficult; for example, the concentrates cannot be pumped out of their storage drums. Together, they result in surfactant networks, which are complex; such networks include micelles, microemulsions, lamellar phases and gels. It is known for example, that "even small amounts of surfactants can, under certain condition, gelify ... water". See H. Hoffman and G. Ebert, Angew. Chem. Int. Ed. Engl., <u>27</u>, p. 902-12 (1988), which is incorporated herein by

reference. Thus, small changes in surfactant mixtures can l ad to dramatic results, due to changes in the makeup of the surfactant networks. Overcoming problems resulting from the formation of surfactant networks is often more of an art than a science.

Concentrates of alkyl aromatic sulfonates are broadly disclosed in the art. For example, U.S. Patent No. 4,743,385 to Angstadt et al., issued May 10, 1988, discloses an improved method of enhanced oil recovery using steam and a composition comprising about a 1:0.05 to 0.5:2.0 weight ratio of a C_{14-20} alkyl aromatic sulfonate (AAS) and a hydrotrope selected from the group consisting of alkali metal xylene sulfonates, alkali metal toluene sulfonates, alkali metal cumene sulfonates, alkali metal benzene sulfonates, alkali metal isethionates, alkali metal butane sulfonates and alkali metal hexane sulfonates. Long chain alkyl groups on the AAS, containing from about 12 to 30 carbon atoms, are broadly taught. This Angstadt patent teaches that mixtures of these alkyl aromatic sulfonates and these hydrotropes, when employed together in a steam recovery process, exhibit unexpected synergistic effects on oil recoveries. A concentrate containing up to 25 wt % hexadecyl toluene sulfonate and 17% sodium xylene sulfonate is disclosed (Col. 5, line 44). This patent generally teaches almost equal weights of the alkyl aromatic sulfonate and the hydrotrope, in order to prepare easily handled solutions.

U.S. Patent No. 3,874,454 to Clark et al. discloses an overbased anionic waterflood additive composition comprising a water-soluble low molecular weight alkali metal hydrocarbon sulfonate having an average equivalent weight of about 200-400 and an oil soluble alkali metal sulfonate

with average equivalent weights of 400-600 and an overbasing amount f a base. This patent also discloses (Col. 5, line 43 et. seq.) the use of "water-soluble solubilizing" agents such as sodium xylene sulfonate or ethoxylated phenols. Concentrates of 15, 25, and 50 wt % are disclosed.

Similarly, U.S. Patent No. 3,933,201 to Kerfoot discloses a water flood additive comprising an overbased, branched, high molecular weight alkyl aromatic sulfonate derived from propylene tetramer dimer containing 20-30 carbon atoms and optionally a water soluble solubilizing agent such as sodium xylene sulfonate. Kerfoot discloses compositions containing up to 25 wt % alkyl aromatic sulfonate, with a weight excess of (neutralizing) base component. This patent also discloses the use of ethoxylated alkyl phenols. See, for example, Col. 6, line 37-60.

All these patents disclose the addition of significant amounts of organic additives relative to the foaming alkyl aromatic sulfonates, both in their teachings and more particularly in their examples. Additionally, although they broadly teach concentrates, the examples are generally directed to formulations containing less than 10 wt % of the alkyl aromatic sulfonate.

However, it is economically undesirable and therefore not practical to add large quantities of additives to these foaming surfactants. Indeed, it is necessary that the organic additive, i.e., the phase stabilizing additives and the viscosity reducing additives, not increase the costs of the surfactant concentrates to such a degree that they eliminate the incentives for producing concentrates. That is, the concentrate formulation containing these additives

must cost less than the shipping costs of dilute alkyl aromatic sulfonates. In this regard, it is d sirabl to minimize the cost of the additive package by r ducing the quantity of additives added, especially since the additives are typically more costly than the foaming alkyl aromatic sulfonates.

Thus, although all these patents teach formulations for alkyl aromatic sulfonates, there is still a need for flowable concentrate compositions of these foaming surfactants which can be easily handled in the field despite being subjected to storage for extended periods or exposure to low temperatures, and which minimize the amount of organic additives employed.

Accordingly, it is an object of the present invention to provide a low cost, flowable concentrate of C_{20-30} alkyl aromatic sulfonates which is not subject to undesirable increases in viscosity when stored, particularly for extended periods and/or after exposure to low temperatures. Furthermore, it is another object of the present invention to provide concentrate formulations that are stable with regard to phase separation. This and other objects will become apparent from the specification and claims which follow.

SUMMARY OF THE INVENTION

The present invention relates to flowable concentrates of C_{20-30} alkyl aromatic sulfonates useful as a foaming agent in enhanced oil recovery operations, and to a method for recovering hydrocarbons from hydrocarbon bearing reservoirs using these concentrates.

In one embodiment, the present invention is a flowabl foaming surfactant concentrate, comprising: (a) greater than 12 wt % of C_{20-30} alkyl aromatic sulfonates having an average molecular weight between about 460 and about 600; (b) a mixture of additives comprising a viscosity-reducing hydrotrope and a dispersant comprising a nonionic surfactant; and (c) water, where this concentrate is a dispersion having a viscosity, as prepared, of less than 3,000 cp at 70°F and a Dispersion Stability Index greater than 2.2, and where this concentrate contains less than 60 wt % of organic additive relative to the foaming alkyl aromatic sulfonate.

Preferably, a hydrophilic nonionic ethylene oxide propylene oxide block copolymer is also included in the concentrate to further improve the dispersion stability. Moreover, the mixture is desirably overbased, for example with sodium bicarbonate, to maintain the sulfonates in salt form.

In another aspect, the present invention relates to a method for preventing the gelling of an aqueous mixture comprising water and a linear C_{20-24} alkyl aromatic sulfonate during storage of the mixture comprising adding of a viscosity-reducing hydrotrope and a nonionic dispersant to the mixture. The viscosity-reducing hydrotrope is preferably added prior to storing and/or transporting the mixture.

In still another aspect, the present invention relates to a method for enhancing the recovery of hydrocarbons from a subterranean hydrocarbon-bearing formation which comprises diluting the flowable concentrates of this invention, periodically injecting gas comprising steam and the diluted concentrate of this invention into the formation to form a

foam, and subsequently recovering oil from the formation. The concentrate comprises water, greater than 12 wt % of a C_{20-30} alkyl aromatic sulfonat , a viscosity-reducing hydrotrope and a dispersant comprising a nonionic surfactant, wherein the hydrotrope and dispersant comprise less than 60% by weight of the alkyl aromatic sulfonate. The alkyl aromatic sulfonate component has an average molecular weight of between about 460 to about 600, is present in an effective foam-forming amount and includes at least one alkyl group comprising between 20-30 carbon atoms. The viscosity-reducing hydrotrope is present in an amount effective to prevent gelling of the mixture and such that the concentrate, as prepared has a viscosity of less than 3000 cp. The nonionic dispersant is present in an amount sufficient to ensure that the Dispersion Stability Index of the concentrate is greater than 2.2.

Among other factors, the present invention is based on our discovery that when high concentrations, such as 20 wt %, of linear C_{20-24} alkyl aromatic sulfonates are mixed with certain unique combinations of viscosity-reducing hydrotropes and nonionic dispersants, the resulting concentrates are flowable, dispersion stable and freeze-thaw stable. Moreover, we have found that the addition of small amounts of certain polymeric nonionic surfactants can virtually eliminate phase separation.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to foam forming surfactant concentrates which can be effectively employed with steam in enhancing the recovery of petroleum from oil bearing formations. These concentrates comprise greater than 12 wt % of a C_{20-30} alkyl aromatic sulfonate, and a mixture

of organic additives comprising a viscosity-reducing hydrotrop and a dispersant comprising a nonionic surfactant. Optionally, a polymeric nonionic surfactant is also added. A preferred alkyl aromatic sulfonate is a mixture of linear C_{20-24} alkyl toluene sulfonates having an average of greater than 20 carbon atoms on the alkyl group. The amount of additives, relative to the alkyl aromatic sulfonate, is less than 60 wt %, preferably less than 50 wt %, and most preferably less than 40 wt %.

It has now been discovered that a unique combination of a linear C_{20-24} alkyl toluene sulfonates with both a viscosity-reducing hydrotrope and a dispersant comprising a nonionic surfactant can produce highly concentrated aqueous dispersions, containing greater than 12 wt %, and preferably greater than 15 wt % of the C_{20-24} alkyl toluene sulfonate. These surfactant concentrates have reduced viscosities and increased physical phase stabilities, i.e., reduced rates of phase separation with a Dispersion Stability Index of greater than about 2.2, and thus provide more homogeneous formulations. Without the nonionic dispersant in the formulation, physical phase stability is tremendously reduced even in the presence of the hydrotrope. The increased physical phase stability with a reduced rate of phase separation possessed by the present novel formulations are surprising and unpredictable.

THE ALKYL AROMATIC SULFONATE

The alkyl aromatic sulfonates useful in this invention have average molecular weights of from about 460 to about 600 more preferably from about 460 to about 550 and most preferably from about 475 to about 525, based on sodium as the cation. This number average molecular weight is

calculated based on the measured molecular weight of the pr cursor alkyl aromatic moiety as determined by vapor pressure osmometry using toluene as the solvent (ASTM D-2503). One hundred and two mass units are added to this measured molecular weight for the SO_3Na group. Thus, the molecular weight of the alkyl aromatic sulfonates is based on sodium as the cation. Adjustments for other cations, such as potassium, ammonium and alkyl ammonium, can readily be calculated.

The alkyl aromatic sulfonate employed in the present invention includes alkyl aromatic sulfonates where the average chain length of at least one of the alkyl groups comprises between 20-30 carbon atoms, preferably between 20-28 carbon atoms, more preferably between 20-24 carbon atoms. The average carbon number of the linear alkyl group is greater than 20. Although the alkyl aromatic sulfonates useful in this invention may be relatively pure compounds, mixtures are preferred. The concentrates of this invention, when injected with steam into oil bearing formations, provide a foam in the presence of residual oil.

Preferably the alkyl aromatic sulfonate has a linear alkyl group. By "linear alkyl group" is meant an alkyl group having mostly secondary carbon atoms ($-CH_2-$). The linear alkyl group can have some branching. However, the degree of branching is such that the linear alkyl group is substantially straight chain, that is, greater than 80 number percent of the individual carbon atoms in the alkyl substituent are either primary ($-CH_3-$) or secondary ($-CH_2-$) carbon atoms, preferably greater than 85%.

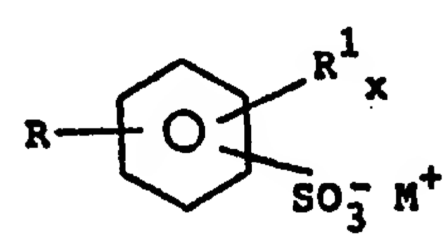
Linear alkyl aromatic sulfonates are readily prepared by reacting linear alpha olefins with aromatic compounds over

acid catalysts, followed by sulfonation. Pr paration methods are well known in the art. Preferred alkylation catalysts are acid catalysts, such as $AlCl_3$ and HF. Sulfonation is preferably accomplished using SO_3 or H_2SO_4.

The composition of the alkyl aromatic sulfonates depends on the composition of the alkylating agent and the aromatic moiety. Useful alkylating agents include alkyl halides and olefins; olefins, especially alpha olefin, are preferred. The starting olefins used to alkylate the aromatic moiety may have a single carbon number, although mixtures of carbon numbers are preferred. Often, mixtures of olefin isomers are used to alkylate the aromatic moiety. Typically, commercially available alpha olefins are mixtures of isomers which include alpha olefins, vinylidene olefins and internal olefins. A preferred linear alkyl group is derived from alpha olefin ethylene oligomerization, such as those sold by Chevron Chemical Company, San Ramon, California.

The aromatic component of the alkyl aromatic sulfonate is selected from the group consisting of benzene, ethyl benzene, toluene, xylene, cumene and naphthalene. Benzene and toluene are especially preferred.

The structure of a preferred linear alkyl aromatic sulfonate of this invention is:



where R is a linear alkyl group having between 20 and 30 carbon atoms, wher R^1 is methyl or ethyl, where x denotes 0-2 such R^1 groups and where M^+ denotes a cation. Examples of preferred linear alkyl groups useful in this invention include mixtures of n-eicosyl, n-heneicosyl, n-docosyl, n-tricosyl, and n-tetracosyl.

The sulfonate component is present as a salt. Preferred cations include sodium, potassium, ammonium or alkyl ammonium. Sodium is especially preferred.

In the concentrates of this invention, the C_{20-30} alkyl aromatic sulfonate is present in an amount of about 12 to about 30% by weight, preferably about 15 to about 25% by weight with 17 to about 23% by weight being most preferred.

THE NONIONIC DISPERSANT

We have now discovered that certain nonionic surfactants selected from the group consisting of alkyl phenol ethoxylates, alcohol ethoxylates, and ethoxylated propylene glycols, are especially effective in increasing the physical phase stability of concentrated, e.g. 20 wt %, aqueous C_{20-24} alkyl toluene sulfonates when formulated with hydrotropes such as sodium xylene sulfonate, or sodium toluene sulfonate.

The nonionic surfactant or dispersant is preferably an alkyl phenol ethoxylate, preferably a nonylphenol ethoxylate. An especially preferred dispersant is represented by the formula $R(OCH_2CH_2)_nOH$, where R is a nonylphenyl group and n is a number from 5 to 15.

The dispersant is added in an amount sufficient to ensure that the Dispersion Stability Index of the concentrate is greater than 2.2, preferably greater than about 3, and more preferably greater than about 5. Typically, the weight ratio of the nonionic surfactant to the alkyl aromatic sulfonate is about 1:40 to 1:10, preferably about 1:15.

Moreover, we have found that it is advantageous to add a polymeric nonionic surfactant or a mixture thereof to further stabilize the dispersion. This polymeric nonionic surfactant or polymeric stabilizing agent preferably has a hydrophile lipophile balance (HLB) value of greater than 7, more preferably greater than 9 and is therefore hydrophilic. HLB values for nonionic surfactants are well known in the art; see for example the description in "Emulsions and solubilization," K. Shinoda and S. Friberg, Wiley - Interscience Publication, 1986, pages 74-82.

Preferred polymeric nonionic surfactants include ethylene oxide (EO) propylene oxide (PO) block copolymer or an alkyl polyglycoside. Preferred EO and PO block copolymers have the EO blocks at the chain ends. Preferred polymer surfactants include Pluronic P103, P104, P105, F68 and F127 and Tetronic 304 sold by BASF Wyandotte Corporation; a preferred polyglycoside is APG 550 sold by Henkel Corporation. Mixtures of polymeric nonionic surfactants may also be used.

The polymeric nonionic surfactant or mixtures thereof, when added, is preferably added in an amount effective to maintain the concentrate as a homogeneous flowable dispersion. Typically, its weight ratio relative to that of the alkyl aromatic sulfonate is about 1:100 to 1:5, preferably about 1:15. We have surprisingly found that

inclusion of a polymeric nonionic surfactant can result in concentrates having a Dispersion Stability Index of about 100, i.e., no or practically no phase separation whatsoever.

THE VISCOSITY-REDUCING HYDROTROPE

Another critical component of the concentrate formulations of this invention is a viscosity-reducing hydrotrope. A hydrotrope is a compound that increases the solubility of a surfactant in water. Hydrotropes are well known in the art, and are low molecular weight alkali metal sulfonates, including both aryl and non-aryl compounds. We have found that they are particularly effective at reducing the viscosity of the concentrates.

In the present invention, a "viscosity-reducing hydrotrope" is added to the mixture. These hydrotropes reduce the viscosity of the resulting mixture to a value of less than about 3000 cp, when the mixtures are first prepared, preferably less than 1500. Useful hydrotropes are those which prevent the gelling of the concentrate during storage, particularly storage over long periods of time and/or after exposure to low temperatures. Hydrotropes which can be employed include sodium xylene sulfonate, sodium toluene sulfonate, sodium hexyl sulfate and sodium octyl sulfate. Preferred viscosity-reducing hydrotropes are sodium xylene sulfonate and sodium toluene sulfonate. Unexpectedly, we found that sodium cumene sulfonate failed to reduce the viscosity to the desired level.

The viscosity-reducing hydrotrope is preferably added in an amount effective to prevent gelling of the concentrate mixture. Desirably, the weight ratio of the hydrotrope to

the alkyl tolu ne sulfonate is in th range of about 1:15 to about 1:1.5, preferably in the range of about 1:6 to about 1:2, more preferably in the range of about 1:5 to about 1:3. Preferably, the hydrotrope is present in the aqueous mixture in an amount of about 4 to about 10% by weight with about 5 to about 8% being more preferred.

It is desirable to produce concentrates with low viscosities, as prepared, because storage and especially freeze-thaw cycles generally result in some viscosity increase.

OTHER COMPONENTS

The water which can be effectively employed within the present invention can include water from any natural source, and can include brines. It is desirable to overbase the concentrates of this invention. This ensures that the sulfonates are present as salts and prevents corrosion of storage containers. Useful overbasing agents are basic, water-soluble, inorganic buffers, such as sodium bicarbonate and sodium carbonate. They are preferably added at 0.5-5 wt %, preferably 1-2 wt %, based on the final weight of the concentrate.

Additionally, other surfactants can be added to our concentrate formulations. These include alpha olefin sulfonates, alpha olefin sulfonate dimers, alkyldiphenylether disulfonates, dialkyldiphenylether disulfonates, alcohol ethoxysulfates, alcohol ethoxy sulfonates, C_{9-18} (preferably C_{12}) alkyl aromatic sulfonates, or mixtures thereof. These are preferably added in amounts ranging from 0-5 wt % of the total concentrate weight, preferably 0-2 wt %.

Preferably, the C_{9-18} alkyl aromatic sulfonates when mployed have a molecular weight of about 300 to less than 450 with an alkyl group comprising 9 to 18 carbon atoms. Most preferably, these alkyl aromatic sulfonates include C_{12} alkyl benzene sulfonates which are either linear or branched, as well as alkyl toluenes, xylenes, cumenes, or naphthalenes. Alternatively, alpha olefin sulfonates (AOS) such as C_{10} to C_{24} AOS, preferably C_{12} to C_{16} AOS, and most preferably C_{12}-C_{14} AOS, or alpha olefin sulfonate dimers such as those exemplified in U.S. Patent 4,556,107 can be used in this invention.

As it is undesirable to dilute the foaming C_{20-30} alkyl aromatic sulfonates with non-foaming additives or additives that are less effective foamers in the presence of residual oil, the concentrates of the present invention contain less than 50 wt % of these organic additives relative to the foaming C_{20-30} alkyl aromatic sulfonate, more preferably less than 40 wt %.

MAKING FLOWABLE CONCENTRATES

Any known method for providing an admixture of water and alkyl aromatic sulfonate can be employed. For example, the water can be mixed with the calculated amount of 50% sodium hydroxide needed to neutralize the alkyl aromatic sulfonic acid -- the dispersant -- such as a nonionic alkyl phenol ethoxylate and the viscosity-reducing hydrotrope. These components are mixed and preferably heated slightly, for example to about 30-70°C, and the alkyl aromatic sulfonic acid is added to the mixture by any known means, for example, by being pumped into the mixture over a controlled period of time. It is desirable to have additional base, such as sodium bicarbonate, in the final mixture to ensure

the mixtur r mains basic during storage. This additional bas can be added at anytim during pr paration of the mixture. Th polymeric nonionic surfactant, such as the block copolymer of ethylene oxide and propylene oxide or the nonionic alkyl polyglycosides -- when employed -- is preferably added prior to addition of the alkyl aromatic sulfonic acid.

In a preferred embodiment of this invention, the alkyl toluene sulfonic acid is added last to an aqueous mixture of sodium hydroxide, sodium bicarbonate, hydrotrope, and dispersant. Efficient mixing during preparation is important so that the resulting mixture is flowable and dispersion stable.

With regard to the use of the term "flowable", we mean a Brookfield viscosity of the mixtures as prepared, of less than about 3,000 cp, measured at 70°F and preferably less than 1,500 cp. In the absence of the herein described additives, viscosities greater than 10,000 cp are often observed when the amount of the C_{20-30} linear alkyl aromatic sulfonate in the mixture is greater than about 10 wt %.

The flowable concentrates of the present invention also have high dispersion stabilities. Dispersion stabilities are measured under defined test conditions (see Example B below) and are based on the ratio of an upper dispersion phase to a lower transparent phase after standing at ambient room temperature for a specified period of time. The dispersion stability index is the ratio of this dispersed upper phase to the transparent lower phase. For C_{20-30} alkyl aromatic sulfonates these dispersions appear to be a dispersion of solids.

The viscosity-reducing hydrotrope can be added either prior to storage of the mixture or it can be added after the mixture has "gelled", if the hydrotrope can be uniformly dispersed in the mixture. It is preferable to add the hydrotrope prior to storage. In either case, when an effective amount of the viscosity-reducing hydrotrope is sufficiently mixed into the mixture, it can provide a flowable dispersion having a viscosity below about 3,000 cp, which will not gel during subsequent storage and/or transporting.

For example, in the method for making the concentrate where the alkyl aromatic sulfonic acid is added to the mixture of water, sodium hydroxide and the nonionic ethoxylate, the viscosity-reducing hydrotrope can either be added prior to the addition of the alkyl aromatic sulfonic acid or after neutralization, preferably before neutralization.

Table A, below, shows the weight ratio of active components, i.e., the weight ratio of the C_{20-30} alkyl aromatic sulfonate (AAS) to the viscosity-reducing hydrotrope to the nonionic dispersant to the polymeric nonionic stabilizing agent or nonionic polymer.

TABLE A

	Broad	Preferred	More Preferred
AAS	12-30	15-25	17-23
Hydrotrope	2-15	4-10	5-8
Dispersant	0.5-2.5	0.75-1.75	1-1.5
Nonionic Polymer	0-5	0.1-2.0	0.5-1.5

Given the range of additives in Tabl A, it is noted that concentrates of this invention additionally meet the proviso that the organic additives, which include the hydrotrope, the dispersant, the nonionic polymer, and any other surfactants besides alkyl aromatic sulfonates, but does not include inactive unreacted unsulfonated alkyl aromatic, are present so that their weight ratio, relative to the AAS is less than 60%, preferably less than 50%, and most preferably less than 40 wt %.

The concentrates of the present invention have a Dispersion Stability Index (DSI) of greater than 2.2, preferably greater than about 3, and more preferably greater than 50. We have succeeded in preparing concentrates with a DSI of 100. The DSI measures the phase separation after standing at ambient room temperature for a specified period of time. The simple test used to determine the value of this Index for a surfactant mixture is described in Example B herein- below. The concentrates of this invention appear to be dispersions or solids or slurries rather than solutions. Indeed, as shown in Example 9 below, the dispersed upper phase contains the majority of the AAS, while the lower transparent phase contains very little of it.

RECOVERING HYDROCARBONS

In another aspect, the present invention is a process for recovering hydrocarbons from a subterranean hydrocarbon bearing formation. This process includes: diluting a concentrate of the present invention; periodically injecting gas comprising steam and the diluted concentrate into the formation to provide a foam; passing the foam into the

formation to assist the movement of hydrocarbons; and recovering hydrocarbons.

Steam-based oil recovery techniques which are preferably used in the present invention include both cyclic and steam drive methods. Each of these methods are well known in the art. Steam-based techniques are particularly preferred for low gravity, high viscosity oil from sedimentary rock formations.

The gas comprising steam employed within the present invention also preferably includes a non-condensible gas such as nitrogen, methane, flue gas, carbon dioxide, carbon monoxide, air, or mixtures thereof, in an amount of 0 to about 50% by volume. A preferred gas is nitrogen. Moreover, the water phase of the steam can include electrolytes such as silicates and sodium chloride in an amount of about 0.1 to about 5% by weight.

In using the concentrate of the present invention for producing oil, the concentrate is preferably diluted with additional water to about 1-0.5 wt % surfactant prior to contact with the steam and injection into the well.

The foam may either be preformed outside the well or "in situ" (i.e., in the formation). In either case, any of the known methods of injecting a foam into the formation may be employed. Desirably, the foam is preformed in the well tubing or formed on the surface, before the mix reaches the well. Most preferably, such foam is preformed by introducing a dilute foam-forming mixture and water into a stream of the gas flowing into the formation through the gas injection well tubing. This ensures foam production before injection into the formation.

The following examples show that our nov l flowable concentrat s do not gel and have desirable low viscosities. We have found that preparing aqueous dispersions with more than about 10-15% of a C_{20-24} alkyl toluene sulfonate requires a hydrotrope and a nonionic dispersant and that a nonionic polymeric stabilizing agent can be advantageously added. Although the following specific examples further illustrate the present invention and the advantages associated therewith, they are merely intended as illustrative, and not to limit the invention in any way.

EXAMPLES

Example A - Viscosity Measurements

The Brookfield viscosity was measured (ASTM D-2983) on about 42 g of sample, allowing 5 minutes for stabilization, using spindle LV 3, at 6 rpm. and expressed in centipoise (cp).

Example B - Determining the Dispersion-Stability Index

Experiments were done using 50 grams of sample in a 4 oz wide mouth jar, or using 20 grams of sample in a 8 dram micro sample vial measuring 25mm in diameter and 95mm in height. When allowed to stand, the formulations generally resulted in some phase separation with a creamy dispersion phase at the top and a transparent phase at the bottom. At 20 wt % alkyl toluene sulfonate (ATS) some phase separation occurred, unless the hydrophilic block copolymer of ethylene oxide and propylene oxide, or the nonionic alkyl polyglycoside was present.

Dispersion stability was tabulated by measuring the depth of the transparent lower liquid phase (in mm) versus the depth

of the upper dispersion phase (in mm) after standing at ambient temperature for a period of 6 hrs. to 10 days. The sum of the two depths totaled 20mm in the wide mouth jar, or 52mm in the 8 dram vial. The smaller the depth of the lower liquid phase and the higher the depth of the upper dispersion phase, the more stable the formulation.

The Dispersion Stability Index (DSI) is the ratio of the depth of the upper dispersion phase to the depth of the lower liquid phase. At very low amounts of lower dispersion phase, i.e., less than 1%, or if there is no separation, the DSI is assigned a value of 100.

Example C - Freeze-Thaw Test Procedure

Freeze-thaw testing was performed by placing 4 oz wide-mouth jars containing 50 g of concentrate measuring 20mm in depth, in a freezer at 22-25F° overnight, removing the jars and allowing them to stand at ambient room temperature for about 5-6 hrs. Brookfield viscosities were measured. This freeze-thaw procedure was repeated up to 8 times. Occasionally the samples were cooled for 2-3 days.

Eight freeze-thaw cycles were performed on the formulations 3-7 and 10-14, see Tables 1-3. The samples were then allowed to stand at ambient room temperature for the indicated time period without disturbance and inspected visually to determine the dispersion stability.

Example 1 - Preparing A Concentrate of this Invention

One hundred grams of surfactant concentrate was prepared by combining 62.34 g of water, 4.74 g of 50% NaOH, 1.60 g of sodium bicarbonate, 1.24 g of Makon 6 and 7.50 g of

40% sodium xylene sulfonate (SXS) in water and shaken by hand for 1-2 minutes. Then 22.58 g of a mixture containing about eighty-five percent C_{20-24} alkyl toluene sulfonic acid and about 15% unreacted impurities was added with stirring. The mixture was then placed on a wrist shaker for 60 minutes. Note: 22.58 wt % C_{20-24} linear alkyl toluene sulfonic acid (84-85% pure) + 4.74 wt % of 50% NaOH gives a C_{20-24} alkyl toluene sulfonate sodium salt (ATS) concentration of 20 wt % in the final formulation. The 7.5 g of 40% SXS solution is about 3 wt % of the final solution.

Fifty grams of this formulation was placed in a 4 oz wide-mouth jar; the mixture measured about 20mm in depth in the jar.

This C_{20-24} linear alkyl toluene sulfonic acid was prepared by sulfonation with sulfur trioxide of a linear alkyl toluene and had an average molecular weight (measured by vapor pressure osmometry on the alkyl toluene in toluene solution) of 494 and an average chain length of about 21 carbon atoms. The alkyl side chain was derived from a C_{20-24} linear alpha olefin. Makon 6, a nonionic surfactant, is a trademark of Stepan Chemical Company (Northfield, Illinois) for a nonylphenol ethoxylate having an average of 6 ethoxy units per molecule. The sodium xylene sulfonate and the sodium toluene sulfonate were obtained from Pilot Chemical Company (Santa Fe Springs, California).

<u>Example 2 - Sample and Comparative Concentrates with SXS</u>

Additional concentrate formulations, as summarized in Table 1, were prepared using sodium xylene sulfonate in the

manner described in Exampl 1. Eight freeze-thaw cycles were performed on formulations 3-7 and 10-14. Viscosity measur ments as shown Table 1 were obtained prior to the freeze-thaw cycles. Formulation C-1 was one of the preferred formulations described in Serial No. 409,595 for a 10% concentrate and is used here for comparison. Doubling the concentration of all the components of formulation C-1 gave Formulation 1 which consisted of 20 wt % of the C_{20-24} alkyl toluene sulfonate as the sodium salt and 1.6 wt % of a C_{12} to C_{18} alpha olefin sulfonate dimer (AOSD). This formulation was very viscous and non-flowable. It was difficult to handle and thus undesirable; it had a Brookfield viscosity of over 68,800 cp. Formulation 2, with a reduction in the amount of AOSD by a factor of 4, did not improve the formulation or reduce the viscosity; it was also undesirable.

Formulation 3, with the introduction of sodium xylene sulfonate added (3 wt %), had a greatly reduced viscosity (from 68,800 cp to 400 cp) and had a separation of 5mm of lower transparent phase after standing for 10 days at ambient room temperature, after 8 freeze thaw cycles (DSI = 15/5 = 3). This was considered desirable.

Formulation 4 without Makon 6 can be contrasted with Formulation 3. It gave a separation of 9mm of clear liquid (DSI = 11/9 = 1.2). This comparison showed the importance of the dispersant, Makon 6 in producing a more stable formulation.

Formulation 5, without AOS Dimer (AOSD), performed similarly to Formulation 3 with AOSD, indicating that AOSD was not necessary in the formulation; it gave a low separation of 5mm of clear liquid (DSI = 15/5 = 3).

Similarly, Formulation 6 without AOSD and without Makon 6 performed poorly with a separation of 9mm of clear liquid. Th c mparison between Formulation 5 and Formulation 6 again indicated that Makon 6 was necessary to decrease the rate of phase separation.

Formulation 7 was similar to Formulation 3, except 0.1 wt % of BASF Pluradyne DB2062, which is a polyol ether, was also added. This formulation had a separation of only 4mm of clear liquid; the viscosity of the mixture increased slightly. Formulation 3-7 all possessed Brookfield viscosities ranging 100-660 cp. Based on these results, it can be seen that Formulations 3, 5, and 7, all of which contained the nonionic dispersant, Makon 6, exhibited decreased rates of phase separation.

Table 1 also summarizes results on test formulations where AOSD has been replaced by a linear C_{12} alpha olefin sulfonate, C_{12}AOS. These formulations, C-2 and 8-14, gave similar results to those described above for C-1 and formulations 1-7. Sodium xylene sulfonate effectively reduced the viscosity of the formulations, and addition of Makon 6 resulted in significantly more stable formulations.

Formulation 14 was similar to Formulation 10 except that 0.1% BASF Pluradyne DB2062 was added. This formulation had a separation of only 2mm of clear liquid, but its viscosity did increase some.

Formulations 10-14 all possessed Brookfield viscosities ranging 140-1,000 cp; they were all flowable. Based on these results, it can be seen that Formulations 10, 12, and 14 -- all of which contain Makon 6 -- exhibited decreased rates of phase separation.

As can b s n by the data in Table 1, the present invention is effective in pr venting th gelling of th mixture, which otherwise would occur as illustrat d by th comparative examples.

Table 2 summarizes Dispersion Stability Index results for Formulations 3-7 after 8 freeze thaw cycles and then after 2, 3, 6, 8, 9, and 10 days of standing at ambient room temperature without disturbance. It also summarizes the Dispersion Stability Index results for Formulations 10-14 after 1, 2, 5, 6, 7, 8, and 9 days of standing at ambient room temperature. Table 2 shows that the rate and amount of phase separation using SXS and Makon 6 was most pronounced during the first 2 days; thereafter, the rate and amount of phase separation decreased dramatically.

Table 3 summarizes the Brookfield viscosity and dispersion stability results for Formulations 3-7 and Formulations 10-14 during their 8 freeze-thaw cycles. The freeze-thaw data show that all these formulations were freeze-thaw stable; they did not form into clumps and had unchanging viscosities during the 8 freeze thaw cycles. These results are highly desirable, because under field conditions these formulations are subjected to alternating freezing and thawing temperatures during the winter season.

Furthermore, in the AOS dimer series, Formulations 3, 5, and 7 containing Makon 6 possessed more dispersion stability than Formulations 4 and 6 without Makon 6. For example, at the third freeze thaw cycle, and after standing for 27 hrs. at ambient room temperature, Formulations 3, 5, and 7 showed only 2mm, 3mm, and 1mm lower liquid phase respectively, whereas Formulations 4 and 6 without Makon 6 both showed 7mm of lower liquid phase.

Similarly, in the C_{12}AOS series, Formulations 10, 12, and 14 with Makon 6 possessed more dispersion stability than Formulations 11 and 13 without Makon 6. For example, at the third freeze thaw cycle, after standing for 6 hours at ambient room temperature, Formulations 10, 12, and 14 showed no separation (i.e., 0mm of lower liquid), whereas Formulations 11 and 13 showed 5mm and 4mm transparent lower liquid phase respectively.

Example 3 - Comparison of Hydrotropes

Test formulations, as summarized in Tables 4 and 5, were formulated in the manner described above in Example 1. In Table 4, hydrotrope sodium toluene sulfonate (STS) was used instead of sodium xylene sulfonate (SXS). In Table 5, hydrotrope sodium cumene sulfonate was used instead of sodium xylene sulfonate. The Brookfield viscosities were measured after the formulations had been made up.

Surprisingly, it was found that not all hydrotropes reduce the viscosity of the 20% C_{20-24} alkyl toluene sulfonate to an equal degree. Hydrotrope sodium cumene sulfonate (SCS) unexpectedly failed to reduce the viscosity to a desirable level.

Table 6 (below) summarizes this comparison of hydrotropes. It shows that, surprisingly, only a selected group of hydrotropes have sufficient viscosity-reducing properties to prevent gelling and thereby allow for easy field handling. As already noted, repeatable (average) Brookfield viscosities of less than 3,000 cps for the concentrates, as prepared, are desirable.

Example 4 - Variations in Number of Ethoxy Groups in Eth xylated Nonylphenol

Test formulations were prepared in a manner similar to that described in Example 1, except that the number of ethoxy group on the ethoxylated nonylphenol was varied, i.e., replacing Makon 6 (6 ethoxy units), with ethoxylated nonylphenols having 5, 9 and 15 ethoxy units. Results for these tests are shown in Table 7. After 5 days at ambient room temperature, Formulations 27, 28, and 29 with an average of 6 ethoxy units (Makon 6) exhibited transparent lower liquid phases of 5mm, 6mm, and 5mm respectively, whereas control Formulations 30 and 31 without Makon 6 exhibited lower liquid phases of 8mm and 9mm. Formulations 32, 33, and 34 with Igepal CO-520 (5 ethoxy units) exhibited lower liquid phase stability of 5mm, 7mm, and 7mm respectively, and were less desirable than those with 6 ethoxy units. Formulations 35, 36, and 37 with Igepal CO-630 (9 ethoxy units) exhibited good dispersion stability with lower liquid phases of 5mm, 3mm, and 2mm respectively. The Brookfield viscosities for these 3 formulations are below 1,200 cp and are desirable. Formulations 38, 39, and 40 with nonionic Igepal CO-730 with 15 ethoxy units exhibited good dispersion stability of 2mm, 2mm, and 1mm respectively after 5 days standing at ambient room temperature. Although the Brookfield viscosities for these latter 3 formulations were slightly higher (800-1,620 cp), they were still acceptable.

Example 5 - Unsuccessful Large Scale Concentrate Preparation Employing 3% Sodium Xylenesulfonate

To a mechanically stirred aqueous solution at 65-70°C in a round bottom flask with paddle was added 50% NaOH (14.2 g),

$NaHCO_3$ (4.8 g), 40% sodium xylenesulfonate (22.5 g), Makon 6 (3.7 g), 40% C_{12}-AOS (3.0 g) and H_2O (184 g). Th n 67.8 g of C_{20-24} linear alkyl toluene sulfonic acid [84-85% active (ai)] was added dropwise. As the addition of the acid progressed, the reaction mixture became very viscous, to a point where inadequate mixing was observed. This experiment indicated that additional amounts of sodium xylenesulfonate were needed, and that effective mixing of the components was necessary for large scale preparations.

Example 6 - Successful Large Scale Concentrate Preparations Employing 6% Sodium Xylenesulfonate

To a fully baffled 4-liter Pyrex resin-reaction kettle equipped with a mechanical stirrer and a 4-bladed radial teflon impeller were introduced H_2O (822 g), 50% NaOH (71.1 g), $NaHCO_3$ (24.0 g), 40% sodium xylenesulfonate (225.0 g) and Makon 6 (18.6 g). The C_{20-24} linear alkyl toluene sulfonic acid (84-85% ai, 339.0 g) was added from a dropping funnel fitted with a piece of Teflon tubing long enough to introduce the acid below the liquid surface, at the level of the mixer blades. The acid was added at a rate to maintain the temperature at 40-50°C and the dropping funnel was warmed as necessary to allow the viscous acid to flow readily into the reaction mixture. The impeller was kept stirring at a rate which minimized air entrainment. After the addition was complete, the reaction mixture was stirred an additional 30 min and then sheared with an Ika Ultra-Turrax disperser. The resulting concentrate had a viscosity below 2000 cp, and had a DSI of 4.2.

Example 7 - Addition of a Polymeric Nonionic Surfactant Stabilizer

A variety of polymeric surfactants were added to aliquots of the mixture of Example 6, or to similar concentrates having 4 wt % SXS. Surfactants tested included anionic and nonionic polymers with molecular weights below about 20,000. Stability results are shown in Table 8. Inclusion of about 1 wt %, based on concentrate weight, of some of these surfactants resulted in completely homogenous dispersions that did not separate after 5 days at room temperature.

The block copolymers of ethylene and propylene oxide (Tetronic, Pluradyne, Pluraflo, and Pluronic trademarks) were obtained from BASF Wyandotte Corporation (Parsippany, New Jersey) and the Tergitol additives from Union Carbide Chemical and Plastics Company (Danbury, Connecticut), and the alkyl polyglycosides were obtained from Henkel Corporation (Ambler, Pennsylvania).

Example 8 - Freeze-Thaw Cycles with EP/PO Block Copolymers

Formulation 144 was prepared in a manner similar to Example 7. The composition containing 20 wt % C_{20-24} alkyl toluene sulfonate, 1.6% $NaHCO_3$, 1.24% Makon 6, 6% SXS and 1.0% Pluronic P104, all percents by weight. The initial viscosity was 2,600 cp. This formulation was subjected to 9 freeze-thaw cycles: Viscosity of 4 cycles was about 3,600 cp, after 9 gels 4,100 cp. Although the viscosity increased as the number of freeze-thaw cycles increased, the product remained flowable and did not separate into phases.

Example 9 - Hyamine Titration of Lower Separated Liquid Phase

One hundred grams of 20 wt % ATS Formulation 114 was allowed to stand at ambient temperature without disturbance for 2 days. The separated lower transparent liquid phase was removed and analyzed by a Hyamine titration (ASTM D 3049). The titration gave a sulfonate content of 1.5% indicating that the majority of the sulfonate was present in the upper dispersion phase (i.e., in the slurry), and that very little sulfonate was dissolved in the lower liquid phase.

While the invention has been described in terms of various preferred embodiments, the artisan will appreciate that various modifications, substitutes, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims including equivalents thereof.

TABLE 1

Form. No.	NOTEBOOK REFERENCE	COMPONENTS, WT % C20-24 ATS	40% AOSD	NaHCO3	Makon 6	SXS	PL'DYNE DB2062	DSI (1)	BROOKFIELD VISCOSITY (2) CENTIPOISE AT 70F	Pass/ Fail
C-1	C0146-16-12	10	2	0.80	0.62	0	0	—	380	P
C-2	C0146-19-11	10	2	0.80	0.62	0	0	—	220	P
1	C0146-16-13	20	4	1.60	1.24	0	0	—	>68,800	F
2	C0146-16-14	20	1	1.60	1.24	0	0	—	68,800	F
3	C0146-16-15	20	1	1.60	1.24	3	0	3.0	400	P
4	C0146-16-19	20	1	1.60	0	3	0	1.2	140	F
5	C0146-16-18	20	0	1.60	1.24	3	0	3.0	440	P
6	C0146-16-17	20	0	1.60	0	3	0	1.2	100	F
7	C0146-16-16	20	1	1.60	1.24	3	0.1	4.0	680	P
			40% C12 AOS							
8	C0146-19-12	20	4	1.60	1.24	0	0	—	>39,600	F
9	C0146-19-13	20	1	1.60	1.24	0	0	—	39,600	F
10	C0146-19-14	20	1	1.60	1.24	3	0	4.0	340	P
11	C0146-19-18	20	1	1.60	0	3	0	1.5	160	F
12	C0146-19-17	20	0	1.60	1.24	3	0	3.0	1000	P
13	C0146-19-16	20	0	1.60	0	3	0	1.5	140	F
14	C0146-19-15	20	1	1.60	1.24	3	0.1	9.0	940	P

(1) After 8 freeze-thaw cycles, and 10 days at ambient temperature
(2) Measured before freeze-thaw cylces

TABLE 2 – Sodium Xylene Sulfonate (SXS) as Hydrotrope

		COMPONENTS, WT %						DISPERSION STABILITY RATIO(1) AFTER X DAYS (2)								
Form. No.	NOTEBOOK REFERENCE	C20–24 ATS	40% AOSD	NaHCO3	Makon 6	SXS	PL'DYNE DB2062	x=1	x=2	x=3	x=5	x=6	x=7	x=8	x=9	x=10
3	C0146–16–15	20	1	1.60	1.24	3	0	NA	4.0	4.0	NA	3.0	3.0	3.0	3.0	3.0
4	C0146–16–19	20	1	1.60	0	3	0	NA	1.9	1.9	NA	1.5	1.5	1.5	1.2	1.2
5	C0146–16–18	20	0	1.60	1.24	3	0	NA	5.7	4.0	NA	4.0	4.0	4.0	3.0	3.0
6	C0146–16–17	20	0	1.60	0	3	0	NA	2.3	1.9	NA	1.5	1.5	1.5	1.2	1.2
7	C0146–16–16	20	1	1.60	1.24	3	0.1	NA	5.7	5.7	NA	4.0	4.0	4.0	4.0	4.0
			40% C12AOS													
10	C0146–19–14	20	1	1.60	1.24	3	0	9.0	5.7	NA	4.0	4.0	4.0	4.0	4.0	NA
11	C0146–19–18	20	1	1.60	0	3	0	3.0	1.9	NA	1.5	2.3	1.5	1.5	1.5	NA
12	C0146–19–17	20	0	1.60	1.24	3	0	9.0	9.0	NA	5.7	5.7	2.4	4.0	3.0	NA
13	C0146–19–16	20	0	1.60	0	3	0	4.0	2.3	NA	1.9	1.9	1.2	1.5	1.5	NA
14	C0146–19–15	20	1	1.60	1.24	3	0.1	19.0	9.0	NA	5.7	9.0	9.0	9.0	9.0	NA

NA = Not available
(1) Ratio of lower phase (in mm) to upper phase (in mm) – 4 oz. wide mouth jar
(2) After 8 freeze–thaw cycles

TABLE 3 – Sodium Xylene Sulfonate (SXS) as Hydrotrope

		COMPONENTS, WT %						NUMBER OF FREEZE-THAW CYCLES								
								0	1	2	3	4	5	6	7	8
Form. No.	NOTEBOOK REFERENCE	C20-24 ATS	40% AOSD	NaHCO3	Makon 6	SXS	PL'DYNE DB2062	BROOKFIELD VISCOSITY, CENTIPOISE AT 70F 1/DISPERSION STABILITY RATIO (number of hours in parenthesis)								
3	C0146-16-15	20	1	1.60	1.24	3	0	400 5/15(41)	300* 2/18(6)	300 <1/19(24)	340 2/18(27)	350* 3/17(24)	400 1/19(7)	380 3/17(24)	360 4/16(48)	400 2/18(6)
4	C0146-16-19	20	1	1.60	0	3	0	140 8/12(41)	120* 2/18(6)	80 4/16(24)	40 7/13(27)	160* 6/14(24)	100 5/15(7)	100 5/15(24)	100 6/14(48)	140 6/14(6)
5	C0146-16-18	20	0	1.60	1.24	3	0	440 6/14(41)	560* 2/18(6)	540 2/18(24)	550 3/17(27)	480* 3/17(24)	650 <1/19(7)	600 3/17(24)	620 3/17(48)	780 3/17(6)
6	C0146-16-17	20	0	1.60	0	3	0	100 8/12(41)	40* 2/18(6)	60 4/16(24)	40 7/13(27)	60* 6/14(24)	100 5/15(7)	100 5/15(24)	60 6/14(48)	80 5/15(6)
7	C0146-16-16	20	1	1.60	1.24	3	0.1	660 4/16(41)	540* <1/19(6)	520 1/19(24)	700 1/19(27)	520* 1/19(24)	560 1/19(7)	380 1/19(24)	520 2/18(48)	600 1/19(6)
			40% C12AOS													
10	C0146-19-14	20	1	1.60	1.24	3	0	340 3/17(43)	360 3/17(24)	350 2/16(24)	400 0/20(6)	440* 1/19(24)	460 0/20(24)	460 <1/19(6)	400 3/17(48)	400 2/16(6)
11	C0146-19-18	20	1	1.60	0	3	0	160 6/14(43)	100 10/10(24)	100 6/14(24)	140 5/15(6)	100* 7/13(24)	140 6/14(24)	100 4/16(6)	100 6/14(48)	100 7/13(6)
12	C0146-19-17	20	0	1.60	1.24	3	0	1000 4/16(43)	900 2/18(24)	840 0/20(24)	920 0/20(6)	900* 1/19(24)	900 2/18(24)	880 0/20(6)	860 3/17(48)	860 2/18(6)
13	C0146-19-16	20	0	1.60	0	3	0	140 6/14(43)	100 7/13(24)	100 5/15(24)	100 4/16(6)	100* 6/14(24)	100 5/15(24)	100 4/16(6)	100 6/14(48)	100 6/14(6)
14	C0146-19-15	20	1	1.60	1.24	3	0.1	940 4/16(43)	800 1/19(24)	800 0/20(24)	900 0/20(6)	900* <1/19(24)	800 0/20(24)	950 0/20(6)	900 <1/19(48)	880 <1/19(6)

* = 2 or 3-day cycle

TABLE 4 - Sodium Toluene Sulfonate (STS) as Hydrotrope

Form. No.	NOTEBOOK REFERENCE	COMPONENTS, WT % C20-24 ATS	40% AOSD	NaHCO3	Makon 6	STS	PL'DYNE DB2062	BROOKFIELD (1) VISCOSITY, CENTIPOISE AT 70F
15	C0227-16-22	20	1	1.60	1.24	3	0.1	400
16	C0227-16-23	20	1	1.60	1.24	3	0	460
17	C0227-16-24	20	0	1.60	1.24	3	0	660
			40% C12AOS					
18	C0227-16-26	20	1	1.60	1.24	3	0.1	500
19	C0227-16-27	20	1	1.60	1.24	3	0	400
20	C0227-16-28	20	0	1.60	1.24	3	0	660

(1) After mixing

TABLE 5 - Sodium Cumene Sulfonate (CSC) as Hydrotrope

		COMPONENTS, WT %						BROOKFIELD (1) VISCOSITY, CENTIPOISE AT 70F
Form. No.	NOTEBOOK REFERENCE	C20-24 ATS	40% AOSD	NaHCO3	Makon 6	SCS	PL'DYN DB2062	
21	C0227-19-12	20	1	1.60	1.24	3	0.1	3,850
22	C0227-19-13	20	1	1.60	1.24	3	0	3,550
23	C0227-19-14	20	0	1.60	1.24	3	0	2,600
			40% C12 AOS					
24	C0146-37-17	20	1	1.60	1.24	3	0.1	4,760
25	C0146-37-18	20	1	1.60	1.24	3	0	1,700
26	C0146-37-19	20	0	1.60	1.24	3	0	3,520

(1) After mixing

TABLE 6

Comparison of Hydrotropes(1)

Formulation Number	Hydrotrope(2)		Viscosity(cp)
23	SCS		3520
26	SCS		2600
		(Avg.)	3060
12	SXS		1000
5	SXS		440
27	SXS		300
		(Avg.)	580
17	STS		560
20	STS		660
		(Avg.)	610
41	none		>40,000
42	none		>40,000

(1) 20 wt % (active) C_{20-24} alkyl toluene sulfonate
3 wt % hydrotrope
1.6 wt % $NaHCO_3$
1.24 wt % Makon 6

(2) SCS=Sodium cumene sulfonate
SXS=Sodium xylene sulfonate
STS=Sodium toluene sulfonate

TABLE 7 – Comparison of Nonyl Phenol Ethoxylates

		COMPONENTS, WT %						BROOKFIELD VISCOSITY,		
Form. No.	EO UNITS (1)	C20–24 ATS	40% AOSD	NaHCO3	ETHOX-YLATE	SXS	PL'DYNE DB2062	CENTIPOISE at 70F (2)	DSI (3)	Pass Fail
27	6	20	0	1.60	1.24	3	0	300	3.0	P
28	6	20	1	1.60	1.24	3	0	520	2.3	P
29	6	20	1	1.60	1.24	3	0.1	700	3.0	P
30	—	20	0	1.60	0	3	0	140	1.5	F
31	—	20	1	1.60	0	3	0	100	1.2	F
32	5	20	0	1.60	1.24	3	0	500	3.0	P
33	5	20	1	1.60	1.24	3	0	400	1.9	F
34	5	20	1	1.60	1.24	3	0.1	340	1.9	F
35	9	20	0	1.60	1.24	3	0	560	3.0	P
36	9	20	1	1.60	1.24	3	0	740	5.7	P
37	9	20	1	1.60	1.24	3	0.1	1150	9.0	P
38	15	20	0	1.60	1.24	3	0	800	9.0	P
39	15	20	1	1.60	1.24	3	0	1220	9.0	P
40	15	20	1	1.60	1.24	3	0.1	1620	19.0	P

(1) Nonylphenol ethoxylates
EO units = 6 is Makon 6 (HLB = 10.8)
EO units = 5 is IGEPAL CO-520 (HLB = 10)
EO units = 9 is IGEPAL CO-630 (HLB = 13)
EO units = 15 is IGEPAL CO-730 (HLB = 15)
(2) After mixing at ambient temperature
(3) After 5 days

Table 8 – Additives Sorted By Dispersion Stability Index (DSI) (1)

Form No.	WT % SXS	NAME OF ADDITIVE	WT %	DSI (2)	TYPE	AVG MW	HLB
100	4	None	0.00	4.8	none		
101	4	Pluronic 10R5	1.00	4.8	block copolymers of EO & PO, nonionic	1950	12-15
102	4	Tetronic 130R2	1.00	4.8	block copolymers of EO & PO, nonionic	7740	3
103	4	Pluradyne 2062	0.50	5.5	polyol ether		
104	4	Poly(Na 4-styrenesulfonate)	1.00	7.7	polymer of styrenesulfonate, anionic		
105	4	Witconate P1059	1.00	7.7	amine salt of dodecyl benzene sulfonate		
106	4	Pluradyne 2062	1.00	18.3	polyol ether		
107	4	Pluronic L62	1.00	25.0	block copolymers of EO & PO, nonionic	2500	7
108	4	Tergitol 15-S-40	1.00	25.0	secondary alcohol ethoxylate, nonionic	1960	18
109	4	Pluradyne DB2042	1.00	49.3	polyol ether		
110	4	Pluradyne DB2065	1.00	100.0	polyol ether		
111	4	Pluronic P104	1.00	100.0	block copolymers of EO & PO, nonionic	5900	13
112	4	Tetronic 304	1.00	100.0	block copolymers of EO & PO, nonionic	1650	16
113	6	Aerosol OTS	1.00	4.2	sulfosuccinate ester, anionic		
114	6	None	0.00	4.2	none		
115	6	None	0.00	4.2	none		
116	6	Macol 15	1.00	4.8	block copolymers of EO & PO, nonionic		15
117	6	None	0.00	4.8	none		
118	6	Polytergent P17A	1.00	6.4	block polymer of EO & PO, nonionic		
119	6	Pluronic L101	1.00	7.7	block copolymers of EO & PO, nonionic	3800	1
120	6	APG 500 Glycoside	1.00	9.4	alkyl polyglycoside, nonionic		11.6
121	6	Emphos PS121	1.00	9.4	phosphate ester, anionic		
122	6	Mazeen C15	1.00	9.4	polyoxyethylene coco amine, cationic		
123	6	Pluronic L64	1.00	9.4	block copolymers of EO & PO, nonionic	2900	15
124	6	Polytergent P17B	1.00	9.4	block polymer of EO & PO, nonionic		
125	6	Polytergent P22A	1.00	12.0	block polymer of EO & PO, nonionic		
126	6	Tergitol 15-S-20	1.00	12.0	secondary alcohol ethoxylate, nonionic	1080	16.3
127	6	Polytergent P32A	1.00	16.3	block polymer of EO & PO, nonionic		
128	6	Pluraflo E4B	1.00	20.0	nonionic		
129	6	Macol 35	1.00	25.0	block polymer of EO & PO, nonionic		8
130	6	Tetronic 304	1.00	25.0	block copolymers of EO & PO, nonionic	1650	16
131	6	APG 550 Glycoside	1.00	33.7	alkyl polyglycoside, nonionic		12.7
132	6	Pluronic P103	1.00	51.0	block copolymers of EO & PO, nonionic	4950	9
133	6	Pluronic P103	1.25	100.0	block copolymers of EO & PO, nonionic	4950	9
134	6	Pluronic F127	1.00	100.0	block copolymers of EO & PO, nonionic	12600	22
135	6	Pluronic F-68	1.00	100.0	block copolymers of EO & PO, nonionic	8400	29
136	6	Pluronic P103	1.50	100.0	block copolymers of EO & PO, nonionic	4950	9
137	6	Pluronic P104	1.25	100.0	block copolymers of EO & PO, nonionic	5900	13
138	6	Pluronic P104	1.50	100.0	block copolymers of EO & PO, nonionic	5900	13
139	6	Pluronic P105	1.00	100.0	block copolymers of EO & PO, nonionic	6500	15
140	6	Tergitol XD	1.00	100.0	copolymer of EO & PO, nonionic	2500	
141	6	Tergitol XH	1.00	100.0	copolymer of EO & PO, nonionic	3500	
142	6	Tetronic 304	1.50	100.0	block copolymers of EO & PO, nonionic	1650	16
143	6	Tetronic 304	1.25	100.0	block copolymers of EO & PO, nonionic	1650	16

(1) Mixtures contain 20 wt % C20-24 ATS, 1.24% Makon 6, 1.6% $NaHCO_3$
(2) Measured after 5 days at ambient temperature

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A flowable foaming surfactant concentrate comprising:

(a) greater than 12 wt % of C_{20-30} alkyl aromatic sulfonates having an average molecular weight between about 460 and 600;

(b) a mixture of organic additives comprising a viscosity-reducing hydrotrope and a dispersant comprising a nonionic surfactant; and

(c) water,

wherein said concentrate is a dispersion having a viscosity, as prepared, of less than about 3000 centipoise at 70°F and a Dispersion Stability Index greater than 2.2, and wherein the amount of said mixture of organic additives is less than 60 wt % of the weight of said C_{20-30} alkyl aromatic sulfonates.

2. The concentrate of Claim 1 wherein said alkyl aromatic sulfonate comprises a mixture of linear C_{20-24} alkyl aromatic sulfonates, and is useful in enhanced oil recovery.

3. The concentrate of Claim 1 wherein said alkyl aromatic sulfonate has an average molecular weight between about 460 to about 550.

4. The concentrate of Claim 2 wherein said alkyl aromatic sulfonate has an average molecular weight of about 475 to about 525.

5. The concentrate of Claim 2 wherein said alkyl group of said linear alkyl aromatic sulfonate is derived from a C_{20-24} alpha olefin.

6. The concentrate of Claim 1 wherein the aromatic component of the alkyl aromatic sulfonate is selected from the groups consisting of benzene, ethyl benzene, toluene, xylene, cumene, naphthalene, and mixtures thereof.

7. The concentrate of Claim 1 wherein the aromatic component of the alkyl aromatic sulfonate comprises benzene or toluene.

8. The concentrate of Claim 1 wherein the alkyl aromatic sulfonate comprises from about 12 to about 30% by weight of the mixture.

9. The concentrate of Claim 1 wherein the alkyl aromatic sulfonate comprises from about 15 to about 25% by weight of the mixture.

10. The concentrate of Claim 1 wherein the viscosity-reducing hydrotrope is selected from the group consisting of sodium xylene sulfonate and sodium toluene sulfonate.

11. The concentrate of Claim 10 wherein the viscosity-reducing hydrotrope is present in an amount of about 2 to about 15% by weight of the mixture.

12. The concentrate of Claim 10 wherein the viscosity-reducing hydrotrope is present in an amount of about 4 to about 10% by weight of the mixture.

13. The concentrate of Claim 10 wherein the viscosity-reducing hydrotrope is present in an amount of about 5 to about 8% by weight of the mixture.

14. The concentrate of Claim 1 wherein the viscosity-reducing hydrotrope comprises about 2 to about 15% by weight of the mixture.

15. The concentrate of Claim 1 wherein the viscosity-reducing hydrotrope comprises about 4 to about 10% by weight of the mixture.

16. The concentrate of Claim 2 wherein the viscosity-reducing hydrotrope comprises about 4 to about 10% by weight of the mixture.

17. The concentrate of Claim 1 wherein the dispersant is selected from the group consisting of alkyl phenol ethoxylates, alcohol ethoxylates, and ethoxylated propylene glycols.

18. The concentrate of Claim 1 wherein the dispersant is an alkyl phenol ethoxylate.

19. The concentrate of Claim 18 wherein the dispersant is a nonylphenol ethoxylate having between 6 and 15 ethoxy groups.

20. The concentrate of Claim 1 further comprising a polymeric nonionic surfactant selected from the group consisting of ethylene oxide propylene oxide block copolymers and alkyl polyglycosides.

21. A concentrate as described in Claim 1 further comprising an ethylene oxide propylene oxide block copolymer having a hydrophilic lipophilic balance (HLB) value greater than 7.

22. A concentrate as described in Claim 21 wherein said ethylene oxide propylene oxide block copolymer has a HLB value greater than 9.

23. The concentrate of Claim 2 wherein the Dispersion Stability Index is greater than about 3.

24. The concentrate of Claim 20 wherein the Dispersion Stability Index is greater than about 50.

25. A concentrate as described in Claim 1 further comprising alpha olefin sulfonates, alpha olefin sulfonate dimers, alkyl diphenylether disulfonates, dialkyl diphenylether disulfonates, alcohol ethoxysulfates, alcohol ethoxysulfonates, C_9-C_{18} alkyl aromatic sulfonates, or mixtures thereof.

26. A concentrate as described in Claim 1 wherein the weight ratio of alkyl aromatic sulfonate to viscosity-reducing hydrotropes is in the range of about 15:1 to about 1.5:1.

27. A concentrate as described in Claim 26 wherein the weight ratio of alkyl aromatic sulfonate to viscosity-reducing hydrotropes is in the range of about 6:1 to about 2:1.

28. A concentrate as described in Claim 26 wherein the weight ratio of alkyl aromatic sulfonate to hydrotropes is in the range of about 5:1 to about 3:1

29. A flowable foaming surfactant concentrate, comprising:

(a) about 20 wt % of a sodium C_{20-24} linear alkyl aromatic sulfonate having an average molecular weight of between 475 and 550;

(b) a mixture of organic additives comprising about 5-8 wt % of a viscosity reducing hydrotrope selected from the groups consisting of sodium xylene sulfonate and sodium toluene sulfonate, a dispersant comprising a nonylphenol ethoxylate having between 5 and 15 ethoxy groups, and an ethylene oxide propylene oxide block copolymer having a hydrophilic lipophilic balance (HLB) value greater than about 9; and

(c) sodium bicarbonate; and

(d) water,

wherein said concentrate is a dispersion having a viscosity, as prepared, of less than 3000 centipoise at 70°F and a Dispersion Stability Index greater than about 50, and wherein the amount of said organic additives is less than 60 wt % of the weight of said C_{20-24} alkyl aromatic sulfonate.

30. A process for recovering hydrocarbons from a subterranean hydrocarbon b aring formati n comprising:

(a) diluting the concentrate of Claim 1;

(b) periodically injecting gas comprising steam and the diluted concentrate of step (a) into said formation to provide a foam;

(c) passing said foam into said formation to assist the movement of hydrocarbons; and

(d) recovering hydrocarbons.

31. The method of Claim 30 wherein the alkyl group of the alkyl aromatic sulfonate of the concentrate of Claim 1 is a linear alkyl group comprising 20 to 24 carbon atoms.

32. The method of Claim 31 wherein the alkyl aromatic sulfonate has an average molecular weight of about 475 to about 525.

33. The method of Claim 30 wherein the viscosity-reducing hydrotropes is selected from the group consisting of sodium xylene sulfonate and sodium toluene sulfonate.

34. The method of Claim 30 wherein the nonionic surfactant is selected from the group consisting of alkyl phenol ethoxylates, alcohol ethoxylates and ethylene oxide propylene oxide block copolymers.

35. A method of preventing the gelling of a surfactant concentrate containing greater than 12 wt % of a C_{20-30}

alkyl aromatic sulfonates having an average molecular weight from about 460-600 and containing a nonionic dispersant comprising the step of adding an antigelling amount of a viscosity-reducing hydrotrope.

36. A surfactant concentrate comprising:

(a) greater than 12 wt % of C_{20-30} alkyl aromatic sulfonates having an average molecular weight between about 460 and 600;

(b) less than 60 wt %, based on the weight of said C_{20-30} alkyl aromatic sulfonates, of a mixture of organic additives, comprising:

(i) a hydrotrope in an amount effective to provide said concentrate, as prepared, with a viscosity of less than about 3,000 centipoise at 70°F and

(ii) a dispersant comprising a nonionic surfactant; and

(c) water,

wherein said concentrate has a Dispersion Stability Index greater than 2.2.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente